

ORIGINAL

Application Based on

Docket **82817HEC**

Inventors: Jin-Shan Wang, Huijuan Chen and Steven Evans

Customer No. 01333

## INK JET INK COMPOSITION

Commissioner for Patents,  
ATTN: BOX PATENT APPLICATION  
Washington, D. C. 20231

Express Mail Label No.: EL656967710US

Date: July 31, 2001

09918584.073101

**INK JET INK COMPOSITION**

**CROSS REFERENCE TO RELATED APPLICATIONS**

Reference is made to commonly assigned, co-pending U.S. Patent

5 Application Serial Numbers:

\_\_\_\_\_ by Chen et al., filed of even date herewith (Docket  
82818), entitled "Ink Jet Printing Method";

\_\_\_\_\_ by Wang, filed of even date herewith (Docket  
83086), entitled "Process for Manufacture of Soluble, Highly Branched  
10 Polyamides, And At Least Partially Aliphatic Highly Branched Polyamides  
Obtained Therefrom";

\_\_\_\_\_ by Wang et al., filed of even date herewith (Docket  
82298), entitled "Water Soluble and Dispersible Highly Branched Polyamides";  
\_\_\_\_\_ by Wang, filed of even date herewith (Docket  
15 82401), entitled "Highly Branched Polyesters Through One-Step Polymerization  
Process"; and

09/697,205 by Wang, filed October 26, 2000, entitled "Highly  
Branched Polyesters Through One-Step Polymerization Process".

**FIELD OF THE INVENTION**

20

This invention relates to an ink jet ink composition comprising a  
hyperbranched polymeric dye comprising a hyperbranched polymer having a dye  
chromophore pendant on the polymer chain or incorporated into the polymer  
backbone.

25

**BACKGROUND OF THE INVENTION**

Ink jet printing is a non-impact method for producing images by  
the deposition of ink droplets in a pixel-by-pixel manner to an image-recording  
element in response to digital signals. There are various methods which may be  
30 utilized to control the deposition of ink droplets on the image-recording element

09918584.073101  
101220"4858T660

to yield the desired image. In one process, known as continuous ink jet, a continuous stream of droplets is charged and deflected in an imagewise manner onto the surface of the image-recording element, while unimaged droplets are caught and returned to an ink sump. In another process, known as drop-on-demand ink jet, individual ink droplets are projected as needed onto the image-recording element to form the desired image. Common methods of controlling the projection of ink droplets in drop-on-demand printing include piezoelectric transducers and thermal bubble formation. Ink jet printers have found broad applications across markets ranging from industrial labeling to short run printing to desktop document and pictorial imaging.

The inks used in the various ink jet printers can be classified as either dye-based or pigment-based. A dye is a colorant which is dissolved in the carrier medium. A pigment is a colorant that is insoluble in the carrier medium, but is dispersed or suspended in the form of small particles, often stabilized against flocculation and settling by the use of dispersing agents. The carrier medium can be a liquid or a solid at room temperature in both cases. Commonly used carrier media include water, mixtures of water and organic co-solvents and high boiling organic solvents, such as hydrocarbons, esters, ketones, etc.

In traditional dye-based inks, no particles are observable under the microscope. Although there have been many recent advances in the art of dye-based ink jet inks, such inks still suffer from deficiencies such as low optical densities on plain paper and poor light-fastness. When water is used as the carrier, such inks also generally suffer from poor water fastness and poor smear resistance. These problems can be minimized by replacing the dyes used in ink formulations with insoluble pigments. In general, pigments are superior to dyes with respect to waterfastness, lightfastness, and stability towards pollutants in the air. However, the pigment inks tend to be unstable and settle out from the liquid vehicle over a long storage time. Pigment inks also have a tendency to clog the orifices of the printhead resulting in deterioration of print quality.

09918584-073101  
TOTEX29-4897660

Accordingly, there is a need for inks having advantages of both dye-based inks and pigment based inks that have good lightfastness, stability towards pollutants, waterfastness and reliability in the printhead.

Polymeric colorants, such as polymeric dyes are known. In  
5 comparison with ordinary colorants, polymeric colorants offer the advantage of allowing a range of physical properties. Their solubility, absorption, migration, and viscosity are tunable and they do not sublime, are non-abrasive, and generally have low toxicity.

U. S. Patent 4,644,708 discloses an ink composition comprising  
10 water and a polymeric dye comprised of the reaction product of a water-soluble polymer with a reactive dye. However, there is a problem with this dye in that its viscosity is high, resulting in poor firability from a thermal ink jet printhead.

U. S. Patent 5,098,475 discloses the preparation of dendrimeric  
15 dyes by reacting a dendrimer with a dye and using the dendrimeric dye in ink formulations. However, there is a problem with these dendrimeric dyes in that dendrimers are typically prepared through lengthy multi-step syntheses, and their availability is limited to a small group of functional monomers.

It is an object of this invention to provide an ink jet ink  
composition that, when printed, provides an image which has improved  
20 waterfastness, lightfastness, and stability towards pollutants such as ozone. It is another object of the present invention to provide an ink jet ink composition that has improved firability through an ink jet printhead.

### SUMMARY OF THE INVENTION

25 These and other objects are achieved in accordance with this invention which relates to an ink jet ink composition comprising water, a humectant, and a hyperbranched polymeric dye comprising a hyperbranched polymer having a dye chromophore pendant on the polymer chain or incorporated into the polymer backbone.

30 It has been found that this ink jet ink composition, when printed, provides an image which has improved waterfastness, lightfastness, and stability

09:13:58.4 "073101  
TOT:20" 48587660

towards pollutants such as ozone and has improved firability through an ink jet printhead.

### DETAILED DESCRIPTION OF THE INVENTION

5 Any hyperbranched polymer may be used in the invention to which is attached a pendant dye chromophore or which has a dye chromophore incorporated into the polymer backbone. A hyperbranched polymer is defined as a polymer formed by polymerization of one or more branching monomers as described in J. Am. Chem. Soc., 74, p2718 (1952), the disclosure of which is  
10 hereby incorporated by reference. In general, hyperbranched polymers can be made through chain polymerization or condensation polymerization processes, as described in U.S. Patent 4,857,630, the disclosure of which is hereby incorporated by reference.

Hyperbranched polymers which may be used in this invention  
15 containing a dye either as a pendant group or in the backbone are described in copending Application Serial No. \_\_\_\_\_ by Wang et al., filed of even date herewith (Docket 82298), entitled "Water Soluble and Dispersible Highly Branched Polyamides" referred to above, and U.S. Patent 6,252,025, the disclosures of which are hereby incorporated by reference.

20 In a preferred embodiment of the invention, the hyperbranched polymer having a dye chromophore pendant thereto which may be used has the formula:



25 wherein:

HB is a hyperbranched polymer core;

D is a dye moiety; and

n is an integer of at least 2.

09918584.073101

In another preferred embodiment, HB is a polyamide, polyester, polyether, vinylic polymer, polyimine, polysiloxane, polyesteramide or polyurethane.

In still another preferred embodiment of the invention, HB is prepared by a chain polymerization of a monomer of the formula  $M^1-R^1-M^2_m$  wherein (i)  $R^1$  is a linear or branched alkyl, carbonyl, or aromatic moiety; (ii),  $M^1$  and  $M^2$  are reactive groups that react independently of each other in which  $M^1$  is a polymerization group and  $M^2$  is a precursor of a moiety  $M^{2*}$  which initiates the polymerization of  $M^1$  as a result of being activated; and (iii), m is an integer of at least 1.

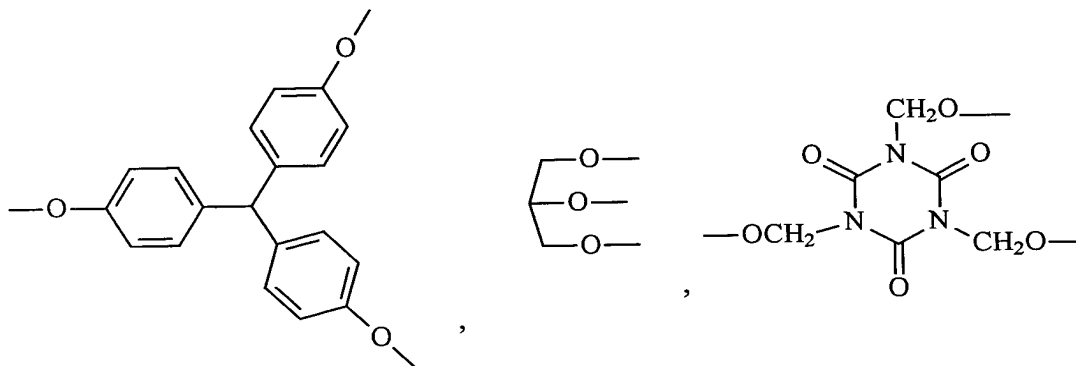
In another preferred embodiment of the invention, HB is prepared by a condensation or addition polymerization of a monomer of the formula  $M^3-R^2-M^4_p$  wherein (i)  $R^2$  is a linear or branched alkyl or aromatic moiety; (ii),  $M^3$  and  $M^4$  are groups that undergo a condensation or addition reaction; and (iii), p is an integer of at least 2.

In another preferred embodiment of the invention, HB is prepared by a condensation or addition polymerization of a monomer of the formula  $R^2-M^5_q$  and  $R^3-M^6_t$  wherein (i)  $R^2$  is as defined above and  $R^3$  is a linear or branched alkyl or aromatic moiety; (ii),  $M^5$  and  $M^6$  are groups that undergo a condensation or addition reaction; and (iii), q is an integer of at least 2 and t an integer of at least 3.

In another preferred embodiment of the invention,  $M^1$  is a non-substituted or substituted vinylic group,  $M^2$  is X,  $-CH_2X$  or  $-CH(CH_3)X$  wherein X is Cl, Br, I, S-C(=S),  $YR^4R^5$  or  $-O-NR^4R^5$ , Y=O or N, and  $R^4$  and  $R^5$  are each independently  $-(CH_2)_r$  (r = 1-12),  $-C_6H_5$ ,  $-C(O)O$ , or C(O).

In another preferred embodiment of the invention,  $M^3$  and  $M^4$  are each independently  $-COOH$ ,  $-OH$ ,  $-C(O)Cl$ , epoxy, anhydride, NH, or  $NH_2$ , and  $R^2$  is  $-C_6H_3-$ , or  $-(CH_2)_s-C(R^6)-$  wherein  $R^6$  is a linear or branched alkyl or aromatic group and s is an integer of 1-12.

In another preferred embodiment of the invention,  $M^5$  and  $M^6$  are each independently  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{C}(\text{O})\text{Cl}$ , epoxy, anhydride,  $\text{NH}$  or  $\text{NH}_2$ ,  $R^3$  is  $-\text{C}_6\text{H}_4-$ ,  $-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-$ ,  $-\text{C}_6\text{H}_3$ ,  $\text{N}(\text{CH}_2)_3-$ ,  $-\text{C}_4\text{H}_8-$ ,  $-\text{C}_6\text{H}_{10}-$ ,



5

The dye chromophores which may be used in the present invention generally include any of the reactive dyes capable of reacting with the hyperbranched polymer to become attached thereto. The bond between the hyperbranched polymer and dye can be a covalent bond or an ionic bond. These dyes typically comprise a chromophore, such as a mono- or poly-azo dye, such as a pyrazoleazoindole dye as disclosed in U.S. Patent Application S.N. 09/689,184 filed October 12, 2000; a basic dye, a phthalocyanine dye, a methine or polymethine dye, a merocyanine dye, an azamethine dye, a quinophthalone dye, a thiazine dye, an oxazine dye, an anthraquinone, or a metal-complex dye, such as those described in U.S. Patents 5,997,622 and 6,001,161, i.e., a transition metal complex of an 8-heterocyclazo-5-hydroxyquinoline.

In still another preferred embodiment of the invention, the hyperbranched polymeric dyes (HBPD) have dye chromophores incorporated into the polymer backbone. These hyperbranched polymeric dyes can be prepared by any kind of polymerization process, similar to those described above for HB. At least one of the monomers used to prepare HBPD contains a dye chromophore.

In a preferred embodiment, the hyperbranched polymer having a dye chromophore incorporated into the polymer backbone is prepared by a chain polymerization of a monomer of the formula  $M^1-R^7-M^2_m$  wherein  $R^7$  is a linear or

branched alkyl, carbonyl, or aromatic moiety containing a dye chromophore and  $M^1$ ,  $M^2$  and  $m$  are defined above.

In another preferred embodiment, the hyperbranched polymer having a dye chromophore incorporated into the polymer backbone is prepared  
5 by a condensation or addition polymerization of a monomer of the formula  $M^3$ - $R^7$ - $M^4$  where  $R^7$ ,  $M^3$ ,  $M^4$  and  $p$  are defined above.

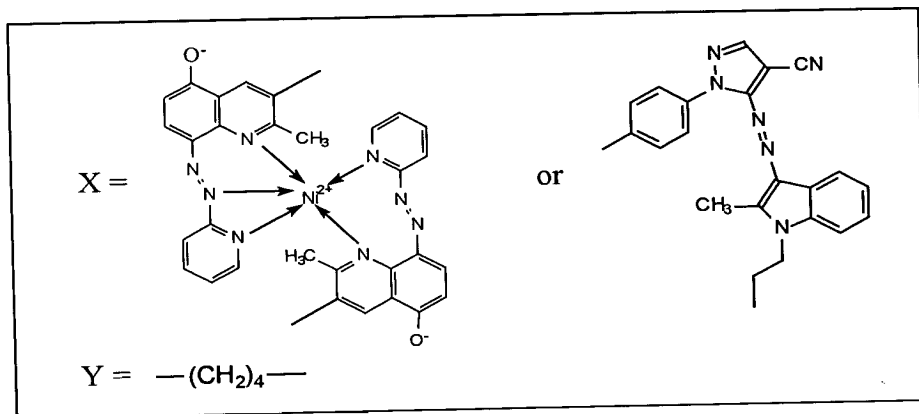
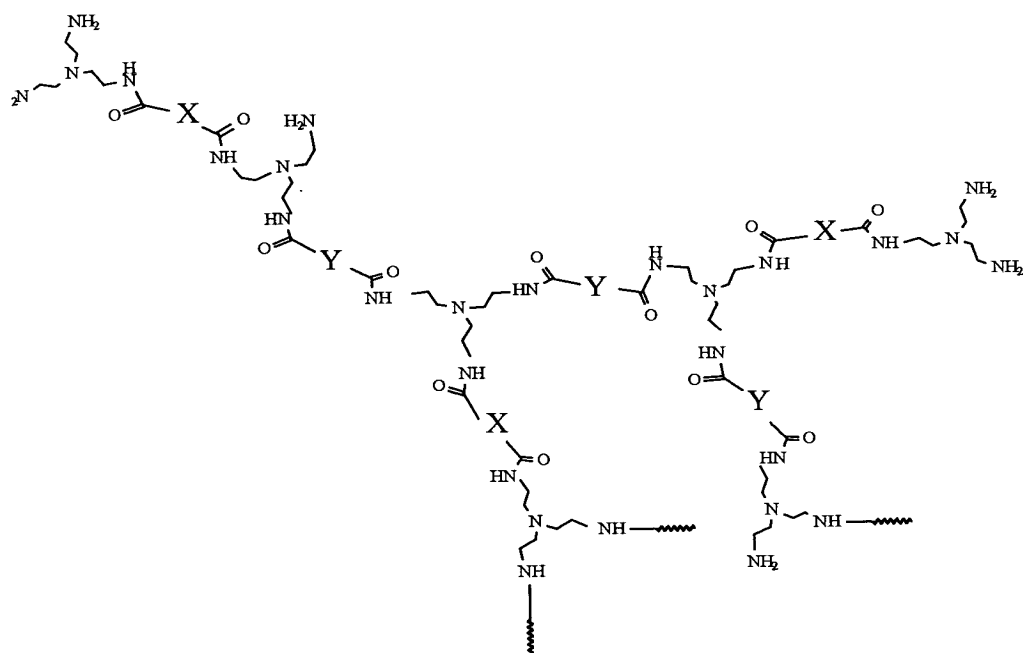
In still another preferred embodiment, the hyperbranched polymer having a dye chromophore incorporated into the polymer backbone is prepared by  
10 a condensation or addition polymerization of a monomer of the formula  $R^8$ - $M^5$  and  $R^9$ - $M^6$  wherein  $R^8$  and  $R^9$  are each independently a linear or branched alkyl or aromatic moiety, at least one of which contains a dye chromophore, and  $M^5$ ,  $M^6$ ,  $q$  and  $t$  are defined as above.

In yet still another preferred embodiment, the hyperbranched polymer having a dye chromophore incorporated into the backbone thereof is a  
15 polyamide, polyester, polyether, vinylic polymer, polyimine, polyesteramide or polyurethane.

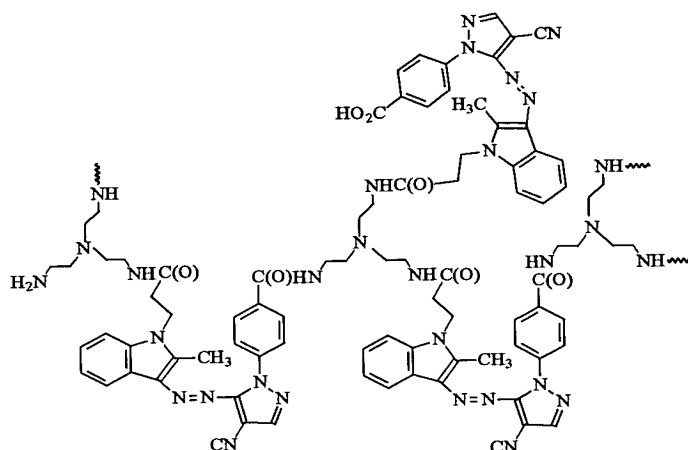
In another preferred embodiment of the invention, the dyes used to prepare the hyperbranched polymeric dyes generally include any of the reactive  
20 dyes with at least two reactive groups capable of reacting with itself (homopolymerization) or with other monomer(s) (copolymerization) to form the hyperbranched polymeric dyes in which dye chromophores are incorporated into the backbone.

Specific examples of hyperbranched polymeric dyes useful in the invention include the following structures:





and



In general, the above hyperbranched polymeric dyes have a molecular weight from about 500 to about 50,000 and comprise from about 0.2 to about 20%, preferably from about 0.5 to 8%, by weight of the ink jet composition.

A humectant is employed in the ink jet composition of the invention to help prevent the ink from drying out or crusting in the orifices of the printhead. Examples of humectants which can be used include polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, 2-methyl-2,4-pentanediol 1,2,6-hexanetriol and thioglycol; lower alkyl mono- or di-ethers derived from alkylene glycols, such as ethylene glycol mono-methyl or mono-ethyl ether, diethylene glycol mono-methyl or mono-ethyl ether, propylene glycol mono-methyl or mono-ethyl ether, triethylene glycol mono-methyl or mono-ethyl ether, diethylene glycol di-methyl or di-ethyl ether, and diethylene glycol monobutylether; nitrogen-containing cyclic compounds, such as pyrrolidone, N-methyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone; and sulfur-containing compounds such as dimethyl sulfoxide and tetramethylene sulfone. A preferred humectant for the composition of the invention is diethylene glycol, glycerol, or diethylene glycol monobutylether.

Water-miscible organic solvents may also be added to the aqueous ink of the invention to help the ink penetrate the receiving substrate, especially

when the substrate is a highly sized paper. Examples of such solvents include alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, iso-butyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol; ketones or ketoalcohols such as acetone, methyl ethyl ketone and diacetone alcohol; ethers, such as tetrahydrofuran and dioxane; and esters, such as, ethyl lactate, ethylene carbonate and propylene carbonate.

Surfactants may be added to adjust the surface tension of the ink to an appropriate level. The surfactants may be anionic, cationic, amphoteric or nonionic.

A biocide may be added to the composition of the invention to suppress the growth of microorganisms such as molds, fungi, etc. in aqueous inks. A preferred biocide for the ink composition of the present invention is Proxel® GXL (Zeneca Specialties Co.) at a final concentration of 0.0001-0.5 wt. %.

The pH of the aqueous ink compositions of the invention may be adjusted by the addition of organic or inorganic acids or bases. Useful inks may have a preferred pH of from about 2 to 10, depending upon the type of dye being used. Typical inorganic acids include hydrochloric, phosphoric and sulfuric acids. Typical organic acids include methanesulfonic, acetic and lactic acids. Typical inorganic bases include alkali metal hydroxides and carbonates. Typical organic bases include ammonia, triethanolamine and tetramethylethylenediamine.

A typical ink composition of the invention may comprise, for example, the following substituents by weight: hyperbranched polymeric dye (0.2-20%), water (20-95%), a humectant (5-70%), water miscible co-solvents (2-20%), surfactant (0.1-10%), biocide (0.05-5%) and pH control agents (0.1-10%).

Additional additives which may optionally be present in the ink jet ink composition of the invention include thickeners, conductivity enhancing agents, anti-kogation agents, drying agents, and defoamers.

The ink jet inks provided by this invention may be employed in ink jet printing wherein liquid ink drops are applied in a controlled fashion to an ink

09918584 "073101

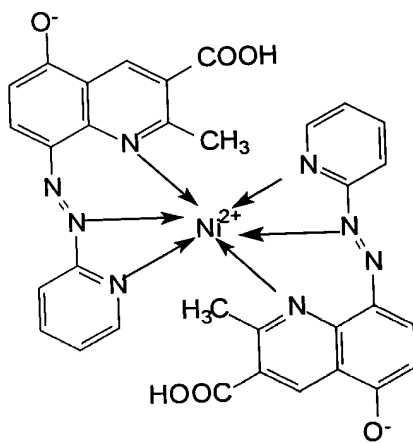
receptive layer substrate, by ejecting ink droplets from a plurality of nozzles or orifices of the print head of an ink jet printer.

Ink-receptive substrates useful in ink jet printing are well known to those skilled in the art. Representative examples of such substrates are disclosed in U.S. Patents 5,605,750; 5,723,211; and 5,789,070 and EP 813 978 A1, the disclosures of which are hereby incorporated by reference.

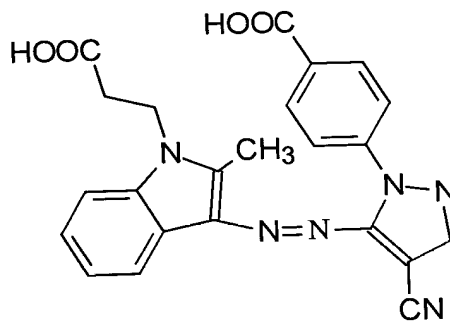
The following example illustrates the utility of the present invention.

### EXAMPLES

The following dyes were used to prepare the hyperbranched polymeric dyes:



Dye 1



Dye 2

#### Synthesis of Hyperbranched Polymeric Magenta Dye HBPD-1

Tris(2-aminoethyl)amine (0.73g), adipic acid (0.35g), and magenta Dye 1 (0.35g) were dissolved in 11:1 1-methyl-2-pyrrolidinone/pyridine (70 wt. % relative to total amount of starting materials). Triphenyl phosphite (100 mol. % of amine) was slowly added into the solution. The reaction mixture was heated

at 80°C for 3 hours under nitrogen. The solution was precipitated from cold ether and purified by dialysis with water using a 1000 MW cut-off bag and followed by freeze drying.

5 Synthesis of Hyperbranched Polymeric Yellow Dye HPBD-2

Tris(2-aminoethyl)amine (0.87g), adipic acid (0.15g), and yellow Dye 2 (0.44g) were dissolved in 11:1 1-methyl-2-pyrrolidinone/pyridine (70 wt. % relative to total amount of starting materials). Triphenyl phosphite (100 mol. % of amine) was slowly added into the solution. The reaction mixture was heated at 80 °C for 3 hours under nitrogen. The solution was precipitated from cold ether and dried at 40 °C under vacuum overnight.

15 Synthesis of Hyperbranched Polymeric Yellow Dye HPBD-3

Tris(2-aminoethyl)amine (0.59g), adipic acid (0.15g), and yellow Dye 2 (0.44g) were dissolved in 11:1 1-methyl-2-pyrrolidinone/pyridine (70 wt. % relative to total amount of starting materials). Triphenyl phosphite (100 mol. % of amine) was slowly added into the solution. The reaction mixture was heated at 80 °C for 3 hours under nitrogen. The solution was precipitated from cold ether and dried at 40 °C under vacuum overnight

20 Synthesis of Hyperbranched Polymeric Yellow Dye HPBD-4

Tris(2-aminoethyl)amine (0.44g), yellow Dye 2 (0.45g) were dissolved in 11:1 1-methyl-2-pyrrolidinone/pyridine (70 wt. % relative to total amount of starting materials). Triphenyl phosphite (100 mol. % of amine) was slowly added into the solution. The reaction mixture was heated at 80 °C for 3 hours under nitrogen. The solution was precipitated from cold ether and dried at 40 °C under vacuum overnight.

Comparative Example 1 (C-1) (Non-polymeric dye)

To prepare a comparative ink jet ink, 0.055 g of Dye 1, 0.05 g Surfynol® 465 (Air Products Inc.), 0.6 g glycerol, 0.1 g triethanolamine, and 1.2 g diethylene glycol were added to 8.05g distilled water. The final ink contained  
5 0.55% dye, 0.50% Surfynol® 465, 6.0% glycerol and 2.0% diethylene glycol. The solution was filtered through a 3 µm polytetrafluoroethylene filter and filled into an empty Hewlett-Packard HP520 ink jet cartridge.

Comparative Example-2 (C-2) (Non-polymeric dye)

10 This ink was prepared similar to Comparative Ink 1 except that Dye 2 was used instead of Dye 1.

Example 1 of the Invention (I-1)

15 This ink was prepared similar to Comparative Ink 1 except that hyperbranched polymeric dye (HBPD-1) was used instead of Dye 1. To prepare this ink, 0.5 g of HBPD-1, 0.05 g Surfynol® 465, 0.6 g glycerol, and 1.2 g diethylene glycol were added to 7.65g distilled water. The final ink contained 5% polymeric dye, 0.50% Surfynol® 465, 6.0% glycerol and 12.0% diethylene glycol. The solution was filtered through a 3 µm polytetrafluoroethylene filter  
20 and filled into an empty Hewlett-Packard HP520 ink jet cartridge.

Example 2 of the Invention (I-2)

This ink was prepared similar to Example1 except that hyperbranched polymeric dye (HBPD-2) was used instead of hyperbranched  
25 polymeric dye (HBPD-1).

Example 3 of the Invention (I-3)

This ink was prepared similar to Example1 except that hyperbranched polymeric dye (HBPD-3) was used instead of hyperbranched  
30 polymeric dye (HBPD-1).

09918584-073101  
TOTAL 4997660

Example 4 of the Invention (I-4)

This ink was prepared similar to Example 1 except that hyperbranched polymeric dye (HBPD-4) was used instead of hyperbranched polymeric dye (HBPD-1).

Printing

Elements were prepared using test images consisting of a series of 21 variable density patches, approximately 15 by 13 mm in size, ranging from 5% dot coverage to 100% dot coverage printed onto commercially available Epson Premium Glossy Paper, Cat. No SO41286, Konica QP Photo IJ Paper (Catalog No. KJP-LT-GH-15-QP PI), Kodak Photographic Quality Paper, Cat. No 800 6298.a with a Hewlett-Packard HP DeskJet® 520 ink jet printer, using the above inks. The elements were allowed to dry for 24 hours at ambient temperature and humidity.

Stability Tests

The above elements were then placed in an ozone chamber (~100 ppb ozone level, 50% relative humidity) for four weeks. Additional elements were subjected to a smear test in a humidity chamber at 38 °C, 80% relative humidity for one week. The Status A reflection densities of the maximum density patch of the elements were measured using an X-Rite® 414 densitometer before and after the fade and smear tests. The percentages of the Status A densities retained for the 100% dot coverage patches were calculated and are listed in Tables 1 and 2. For the smear test, a percentage of density retained higher than 100% indicates that there is a smear problem, and the deviation from 100% shows the degree of smear.

**Table 1**

Element Containing Example Ink	Receiver	Ozone Test (% Retained)
C-1	Epson Premium Glossy Paper	52
C-1	Konica QP	53
I-1	Epson Premium Glossy Paper	88
I-1	Konica QP	73

**Table II**

Element Containing Example Ink	Receiver	Smear Test (% Retained)
C-2	Kodak Photographic Quality Paper	167
C-2	Konica QP	123
I-2	Kodak Photographic Quality Paper	102
I-2	Konica QP	104
I-3	Kodak Photographic Quality Paper	96
I-3	Konica QP	100
I-4	Kodak Photographic Quality Paper	97
I-4	Konica QP	105

5

The above results show that the elements of the invention had improved ozone stability and smear resistance as compared to the control elements.

10 The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.